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(74) Agent: WESTBY, Timothy, S.; CONLEY ROSE, P.C.,  
P.O. Box 3267, Houston, TX 77253-3267 (US).

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(71) Applicant: SYNFUELS INTERNATIONAL, INC.  
[US/US]; Suite 1801, 200 Crescent Court, Dallas, TX  
75201 (US).

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(72) Inventors: JOHNSON, Marvin, M.; 4413 Woodland  
Road, Bartlesville, OK 74006-5340 (US). PETERSON,  
Edward, R.; 3003 Elsbury Lane, Pearland, TX 77584  
(US). GATTIS, Sean, C.; 4830 Scot Court, Sugar Land,  
TX 77479 (US).

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(54) Title: CATALYST FORMULATION FOR HYDROGENATION

(57) Abstract: A composition and method for preparation of a catalyst for the liquid phase selective hydrogenation of alkynes to alkenes with high selectivity to alkenes relative to alkanes, high alkyne conversion, and sustained catalytic activity comprising a Group VIII metal and a Group IB, Group IIB, Group IIIA, and/or Group VIIB promoter on a particulate support.



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## CATALYST FORMULATION FOR HYDROGENATION

### BACKGROUND OF THE INVENTION

#### Field of the Invention

This invention relates generally to novel catalysts for the selective hydrogenation of unsaturated compounds. In particular, the catalyst of the invention preferably contains a Group VIII (using the CAS naming convention) metal and a promoter element, which may be chosen from the groups that contain silver, gallium and indium, manganese, and zinc.

#### Description of the Related Art

Hydrogenation of alkynes and/or multifunctional alkenes to compounds containing only one alkene group is an important industrial process and is discussed widely in the patent literature. Acetylene, the simplest alkyne, occurs in many processes as a main product or by-product which is thereafter converted to ethylene or ethane by hydrogenation. Thermal cracking of ethane can be caused to produce mostly ethylene, but a minor undesired product is acetylene. Pyrolysis of simple alkanes or mixtures containing primarily alkanes and partial oxidation of simple alkanes or mixtures containing primarily alkanes can be made to produce various blends that contain as principal products both alkenes and alkynes. Products in lower abundance will often include diolefins, compounds containing both yne and ene functionalities, polyenes, and other unsaturated moieties. Most commonly the desired products are the singly dehydrated compounds containing a single ene functionality. Thus, it is desirable to convert the alkynes to alkenes, but not convert the desired alkenes further to alkanes. Reactions of alkenes are generally more controllable than those of alkynes and diolefins, which tend to create oligomers and undesirable polyfunctional compounds.

The hydrogenation step is normally carried out on the primary gas produced in the cracking or pyrolysis reaction of natural gas and low molecular weight hydrocarbons, which includes all the initial gas products, also known as "front-end" hydrogenation, or subsequent to fractionation of the gas components, wherein the only stream subjected to hydrogenation is enriched in the highly unsaturated compounds, also known as "tail-end" hydrogenation. The advantage of primary gas hydrogenation is generally an abundance of the hydrogen required for hydrogenation. However, the excess available hydrogen in front-end hydrogenation can result in "run-away" reactivity wherein conversion of alkenes to alkanes reduces the value of the product. Fractionation reduces the available hydrogen but polymer formation is common, the effect of which is to shorten the useful life of the catalyst.

There are numerous examples of gas-phase hydrogenation of alkynes. For example, U.S. Patent No. 6,127,310 by Brown, et al. teaches that the selective hydrogenation of alkynes, which frequently are present in small amounts in alkene-containing streams (e.g., acetylene contained in

ethylene streams from thermal alkane crackers), is commercially carried out in the presence of supported palladium catalysts in the gas-phase.

In the case of the selective hydrogenation of acetylene to ethylene, preferably an alumina-supported palladium/silver catalyst in accordance with the disclosure in U.S. Patent No. 4,404,124 and its division U.S. patent 4,484,015 is used. The operating temperature for this hydrogenation process is selected such that essentially all acetylene is hydrogenated to ethylene (and thus removed from the feed stream) while only an insignificant amount of ethylene is hydrogenated to ethane. Proper temperature selection and control results in minimization of ethylene losses and allows one to avoid a runaway reaction, which is difficult to control.

U.S. Patent No. 5,856,262 describes use of a palladium catalyst supported on potassium doped silica wherein acetylene ranging in concentration from 0.01% to 5% in blends of ethylene and ethane is converted to ethylene in the gas-phase. U.S. Patent No. 6,350,717 describes use of a palladium-silver supported catalyst to hydrogenate acetylene to ethylene in the gas-phase. The acetylene is present at levels of 1% in a stream of ethylene. U.S. Patent No. 6,509,292 describes use of a palladium-gold catalyst wherein acetylene contained in a stream of principally ethylene, hydrogen, methane, ethane and minor amounts of carbon monoxide converts acetylene to ethylene in the gas-phase.

U.S. Patent No. 6,395,952 describes recovery of olefins from a cracked gas stream using metallic salts and ligands. The cracked gas stream is hydrogenated prior to scrubbing to remove acetylene from the stream.

U.S. Patent No. 5,587,348 describes hydrogenation of  $C_2$  to  $C_{10}$  alkynes contained in comparable streams of like alkenes over a supported palladium catalyst containing fluoride and at least one alkali metal. Examples show hydrogenation of low concentrations of acetylene, below 1%, being converted to ethylene in a gas principally comprised of methane and ethylene at 200 psig and 130°F and 180°F. Care was taken to avoid heating the gas to a runaway temperature, wherein at least 4.5% of the ethylene would be converted to ethane and the temperature would become uncontrollable, which varied from about 70°F to 100°F above the minimum temperature that would reduce the acetylene concentration to acceptable levels.

U.S. Patent No. 6,578,378 describes a complex process for purification of ethylene produced from pyrolysis of hydrocarbons wherein the hydrogenation follows the tail-end hydrogenation technique. At the top of the de-ethanizer the vapor of the column distillate is treated directly in an acetylene hydrogenation reactor, the effluent containing virtually no acetylene being separated by a distillation column called a de-methanizer, into ethylene- and ethane-enriched tail product. The vapor containing acetylene is exposed to selective hydrogenation to reduce acetylene content of the

principally ethylene gas or treated with solvent to remove it and preserve it as a separate product. In all cases the acetylene content of the pyrolysis gas contained less than 1.5 mol% acetylene.

Hydrogenation is also known to occur in the liquid phase where the fluids are easily conveyed or transported as liquids under reasonable temperature and pressure. Naphtha cracking produces significant quantities of C<sub>4</sub> and C<sub>5</sub> unsaturated compounds, with 1,3 butadiene and 1-butene generally having the greatest commercial value.

U.S. Patent No. 6,015,933 describes a process in which polymer by-products from the steam cracking of naphtha to butadiene are removed. Acetylenes in the liquid hydrocarbon stream are selectively hydrogenated in a reactor to produce a reactor product containing at least hydrogen, butadiene, and polymer by-products having from about 8 to about 36 carbon atoms, and typically containing butenes and butanes. The acetylenic compounds are primarily vinyl acetylene, ethylacetylene, and methylacetylene. These acetylene group-containing molecules are converted to 1,3 butadiene, 1-butene, and propylene, but can react further with butadiene to form polymeric by-products. The reaction is carried out in the liquid phase with butadiene as the carrier. The undesirable feature of this process is that the carrier reacts with the products of the hydrogenation reaction, necessitating the removal of the polymeric by-products described.

U.S. Patent No. 5,227,553 describes a dual bed process for hydrogenating butadiene to butenes. This improvement is said to increase selectivity in streams containing high concentrations of butadiene while reducing the isomerization of butene-1 to butene-2, and nearly eliminating the hydrogenation of isobutene to isobutane as well as oligomerization.

U.S. Patent No. 4,547,600 discloses the need for more silver than previously thought necessary in the hydrogenation of acetylenic compounds that are found in butadiene as a result of steam cracking. The reaction is performed in the liquid phase where the product is the carrier.

U.S. Patent No. 3,541,178 reports a reduction in the loss of butadiene along with nearly complete reduction of acetylenic compounds by restricting the flow of hydrogen to no more than 80% to 90% of saturation in the hydrocarbon stream. This reduces the potential for polymerization of the vinylacetylenes, as there is no hydrogen remaining in the reaction stream at the end of the reaction. The undesirable aspect of this reduced hydrogen content however, is that the concentration of the hydrogen in the reactor is reduced, which decreases the reaction rate.

U.S. Patent No. 3,842,137 also teaches a reduction in the loss of butadiene to butene along with nearly complete conversion of vinylacetylene to butadiene, through the use of an inert diluent gas for the hydrogen. The hydrogen-containing gas includes no more than 25% hydrogen. The reaction takes place in the liquid phase, between a temperature of 40°F and 175°F, and at a pressure

of 80 to 200 psig. Again however, an undesirable aspect of using a diluent is that concentration of the hydrogen in the reactor is reduced, which decreases the reaction rate.

U.S. Patent No. 4,469,907 teaches high conversions of multiply unsaturated hydrocarbons to singly unsaturated hydrocarbons without subsequent isomerization, by staging the insertion of hydrogen into one or more reactors in series. An undesirable aspect of using several reactors however, is the increased complexity of the process, resulting in increased cost and more complicated process control.

There are several examples where non-linear and/or non-hydrocarbon compounds are hydrogenated in the liquid phase. For example, U.S. Patent No. 5,696,293 describes liquid phase hydrogenation and amination of polyols, carried out at pressures below 20 MPa using a supported ruthenium catalyst and containing another metal from Groups VIA, VIIA, and VIII. A ruthenium-palladium or singly palladium catalyst is listed in the examples. An undesirable feature of this process is the need to filter the fine and expensive catalyst out of the product. Catalyst losses are potentially very costly.

U.S. Patent No. 5,589,600 discloses hydrogenation of benzene to cyclohexene using ruthenium-nickel catalysts in the presence of water, which is purported to improve selectivity. U.S. Patent No. 5,504,268 discloses hydrogenation of aromatic acetylenic compounds that are impurities in vinyl aromatic compounds, over a supported palladium catalyst. The purported improvement is obtained via reduction of the hydrogen concentration by using a gas phase diluent such as nitrogen or methane. As previously noted, an undesirable aspect of using a diluent however, is the reduction in the concentration of hydrogen in the reactor and corresponding decrease in the reaction rate.

Carbon monoxide is known to enhance hydrogenation selectivity. It is added to a stream that has been thermally cracked or pyrolyzed to reduce the hydrogenation of the ene functional groups. U.S. Patent No. 6,365,790 describes an approach to selective hydrogenation of C<sub>10</sub> to C<sub>30</sub> alkynes to their respective alkenes in the liquid phase, by careful addition of a compound that decomposes to form CO. An undesirable aspect of using an additive is that the additive must later be removed from the product in diminished form.

U.S. Patent No. 4,517,395 indicates that CO and H<sub>2</sub> added to a liquid phase of C<sub>3+</sub> multi-ene or mono-yne hydrocarbons, dispersed in the single-ene containing hydrocarbons, results in improved conversion due to better selectivity. The emphasis is on maintaining sufficient pressure to hold the CO and H<sub>2</sub> in the liquid phase rather than dispersed as a heterogeneous phase. Notably, water is added to reduce the amount of CO required as well as to reduce the temperature required.

U.S. Patent No. 4,705,906 presents a catalyst formulation wherein acetylene is converted by hydrogenation to ethylene, in the presence of CO in concentrations greater than 1 vol% in a

temperature range between 100°C and 500°C. The catalyst is a zinc oxide or sulphide, which may incorporate chromium, thorium, or gallium oxide. Zinc oxide and zinc sulphide were reportedly chosen for the reason that, although palladium catalysts are reasonably tolerant of the usual organic impurities which act solely as activity moderators, palladium catalysts are poisoned at low temperatures by high concentrations of carbon monoxide, such as those associated with unsaturated hydrocarbon-containing products obtained by the partial combustion of gaseous paraffinic hydrocarbons. This is to be contrasted with their behavior at low carbon monoxide concentrations, typically at concentrations less than 1 vol%, at which moderation of catalytic activity is reported to enhance the selectivity of acetylene hydrogenation to ethylene. At high temperature, palladium catalysts are active even in the presence of carbon monoxide, but selectivity of acetylene hydrogenation to ethylene is drastically reduced by simultaneous hydrogenation of ethylene to ethane.

In U.S. Patent No. 4,906,800, a Lindlar catalyst was used with a feed that contained no CO. The catalyst contained 5% palladium on a  $\text{CaCO}_3$  support with about 3% lead as a promoter. After special treatment involving oxidation, reduction in CO, and finally a heat treatment step of the readily oxidized and reduced Lindlar catalyst, the treated catalyst showed improved selectivity at high conversion, but again at higher temperatures above 200°C selectivity decreased significantly.

U.S. Patent No. 5,847,250 describes a supported palladium catalyst employing a "promoter" from Groups 1 or 2 (in the New classification system; CAS Groups IA and IIA) and the palladium being supported on silica that has been pretreated to contain the promoter. The purported advantage is that no carbon monoxide is needed to provide increased selectivity because the selectivity-increasing effect of the carbon monoxide is strongly temperature dependent. Large temperature gradients in the catalyst bed therefore have an adverse effect on the selectivity when carbon monoxide is present. The reaction is performed in the gas phase in one or more beds with or without intermediate cooling or hydrogen gas addition. Acetylene content ranges from 0.01% to 5%. The reported selectivity ranges from 19 to 56%.

The use of liquid carriers has also been described in several patents for various reasons. For example, U.S. Patent No. 4,137,267 describes the hydrogenation of alkyl aminopropionitrile in the liquid phase, using hydrogen and ammonia as reactants over a supported catalyst and using an organic solvent. The solvent was selected to absorb excess heat by vaporizing at the process conditions, which is said to provide some temperature control. An undesirable aspect of employing a volatilizing solvent is the concomitant difficulty of employing this technique in a fixed catalyst bed.

U.S. Patent No. 5,414,170 teaches selective hydrogenation of a stream from an olefin plant after operation of a depropanizer but prior to operation of a de-ethanizer or de-methanizer. The hydrogenation is performed on the mixed-phase propane rich ethylene stream, as well as subsequently on the vapor product. A method is described by which the acetylenes in the front end of an olefin plant process stream are hydrogenated in the presence of a liquid hydrocarbon. The propane liquids, initially separated out of the inlet process stream, are used later to cool and wash the product of the acetylene hydrogenation reactor by adding them to the acetylene-containing stream during hydrogenation. An undesirable aspect of this process is the need to fractionate the propane from the small amount of ethylene produced.

U.S. Patent No. 5,059,732 discloses a process to hydrogenate effluent from a steam cracker containing ethylene, acetylene, propylene, propyne, propadiene, and butadiene, with hydrogen in the presence of a palladium or other noble metal catalyst by use of a gasoline cut as an inert carrier. The rationale for improved catalyst life is that the aromatic content of the gasoline carrier prevents plating out of the diolefins on the catalyst, which can otherwise polymerize and form gums that obstruct the other reactive components from getting to the catalyst surface. An undesirable aspect of this process however, is the need to fractionate the heavier hydrocarbon fraction from the small amount of ethylene produced, although this is not as serious a problem as when propane is used as the carrier.

Several patents disclose the use of solvents to separate the acetylenic fraction of a fluid stream from the other components. It is well known that dimethylformamide (DMF) and n-methyl-2-pyrrolidone (NMP) are good liquid absorbents for acetylene. Likewise, it is well known that DMF, furfural, ethylacetate, tetrahydrofuran (THF), ethanol, butanol, cyclohexanol, and acetonitrile are useful absorbents for 1,3-butadiene.

French Patent No. 2,525,210 describes a method for the purification of a stream containing mostly ethylene with a smaller amount of acetylene contaminant, wherein the acetylene is not converted to ethane. The basic concept is to hydrogenate a gas stream short of complete conversion, leaving some acetylene in the gas stream, then to absorb the acetylene in a solvent that extracts the acetylene from the ethylene stream. This extracted acetylene is separated from the solvent and recycled to the ethylene stream for hydrogenation. This is said to increase conversion to ethylene. An undesirable aspect of this process is the need to control the hydrogenation significantly below complete conversion.

U.S. Patent No. 4,277,313 focuses on the purification of a C<sub>4</sub> stream containing acetylenic compounds by hydrogenation of the acetylenic compounds followed by downstream separation. The hydrogenation step is carried out in the liquid phase after the hydrocarbon has been separated from

the absorbing solvent. It is said to be important to remove the acetylenic compounds prior to polymerization since they can form explosive metal acetylides and will cause the polymer to be off-spec. Suitable inert solvents for this process purportedly include: dimethylformamide (DMF), furfural, ethylacetate, tetrahydrofuran (THF), ethanol, butanol, cyclohexanol, and particularly acetonitrile.

U.S. Patent No. 3,342,891 describes fractionating a stream of C<sub>4</sub> and C<sub>5</sub> alkadienes into two streams, where one stream is reduced in vinyl acetylenes and the second stream is enriched in vinyl acetylenes. DMSO was used to separate the vinylacetylene from the enriched stream. The DMSO that contains the vinylacetylene was stripped with nitrogen to concentrate the vinylacetylene, which was subsequently hydrogenated in the gas phase. Unconverted vinyl acetylene in the effluent is recycled back to the feed of the fractionation column.

In some examples, the use of a liquid carrier or solvent is disclosed in which the liquid carrier or solvent is present during the hydrogenation step. U.S. Patent No. 4,128,595 for example, teaches a process wherein gaseous acetylene or acetylene group containing compounds are contacted with hydrogen via an inert saturated liquid hydrocarbon stream with hydrogenation occurring over a typical Group VIII metal supported on a catalyst medium. Examples of inert saturated hydrocarbons include various hexanes, decanes and decalin. The process requires the acetylene containing compound and saturated hydrocarbon solvent be fed co-currently into the top of a trickle bed reactor because the solubility of the acetylene containing compound in the saturated hydrocarbon solvent is poor at reaction conditions. An undesirable aspect of this process is the poor solubility of the hydrocarbon solvent toward acetylene. This patent teaches that rapid catalyst deactivation can occur with polar solvents. Dimethylformamide (DMF) was used as an absorbent for ethylene and the polar solvent during hydrogenation. The result indicated rapid catalyst deactivation with conversion dropping from 100% to 50% over a period of 17 hours. Accordingly, there is substantial need for a practicable liquid phase hydrogenation process, using non-hydrocarbon solvents, with supported palladium-based catalysts, if these could be developed with sufficient activity and selectivity.

Combinations of Group VIII catalysts with Group IIIA metals are found in the art for various applications. French Patent No. 2,091,114 and U.S. Patent No. 6,315,892 describe a catalyst and process respectively in which a palladium/indium supported catalyst was used to dehydrogenate and reform petroleum liquids. This patent discloses the use of a palladium/indium supported catalyst for hydrogenation, which is the reverse chemical reaction.

U.S. Patent No. 5,356,851, EP 564,328, and EP 564,329 describe palladium/gallium catalyst and teach that the group IIIA metal must be deposited on the support before the group VIII metal to achieve superior activity and selectivity for hydrogenation. An undesirable aspect of this method is



that the catalyst cannot be formulated as an existing Group VIII catalyst subsequently modified to impart the group IIIA promoter functionality.

U.S. Patent No. 6,465,391 describes a catalyst that contains palladium, silver, and an alkaline metal fluoride compound, wherein the metal is chosen from the group of antimony, phosphorus, boron, aluminum, gallium, indium, thallium, and arsenic, for hydrogenation of acetylene in a gas stream that contains about 1.25% acetylene in ethylene. However, this catalyst formulation exhibits a selectivity to ethylene of less than 80% in all reported cases.

U.S. Patent No. 5,866,734 describes a catalyst formed from sputtering metals onto a metal mesh support. Specific examples for hydrogenation include palladium, palladium/silver, and palladium/magnesium on wire mesh supports. Some of the undesirable aspects of using wire or foil meshes are that they are difficult and expensive to manufacture, and generally have limited regeneration temperatures and therefore uses.

U.S. Patent No. 6,255,548 and U.S. Patent No. 6,281,160 describe a process for hydrogenation and a process to manufacture a catalyst respectively, whereby a Group VIII metal and metal M, selected from germanium, tin, lead, rhenium, gallium, indium, gold, silver, and thallium are deposited on a support for the purpose of the hydrogenation of acetylenic compounds or diolefins. The deposition of the metal M is accomplished by solubilizing an organometallic compound of M that is soluble in water. An example is presented for a palladium/tin catalyst formed using tributyltin acetate. The resulting catalyst is used to convert isoprene in heptane to n-methylbutene with 98% selectivity.

U.S. Patent No. 4,337,329 relates to a supported catalyst on which palladium and a metal from groups IA, IIA, IIIA, IVA, VA, VIA, as well as germanium and antimony are deposited, for hydrogenating carbon-carbon double bonds of a conjugated diene polymer. An undesirable aspect of using a supported catalyst to hydrogenate a polymer, even a low molecular weight polymer, is the difficulty of recovering the catalyst once the hydrogenation is complete.

U.S. Patent No. 4,323,482 discloses formulation of a catalyst from a metal oxide mixture where one component is reducible and the other is not reducible under selected process conditions. The resulting catalyst has reduced crystallite character which enhances activity. An undesirable aspect of this catalyst preparation is that subsequent processing or regeneration at high temperatures in a reducing atmosphere will tend to cause the catalyst crystallinity to continuously increase.

As is apparent, an efficient, practicable process for liquid-phase selective hydrogenation, using a catalyst with sufficient activity and selectivity, would be a substantial contribution to the art. It has now been found that significant improvements in the selectivity to ethylene can be obtained from the addition of promoters at high acetylene conversion in accordance with the present

invention. Surprisingly, and contrary to the teachings of the conventional art relating to use of a polar solvent, such as dimethylformamide, a progressive decline in catalyst activity with time on stream is not observed with the present invention. Further, gallium and indium promoted catalysts of this invention exhibited satisfactory selectivity. Additionally, and contrary to the teachings of the prior art, excellent selectivity and activity results were obtained using a catalyst formed by first applying a Group VIII metal to the support and then subsequently applying a Group IIIA metal.

### SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and to provide a catalyst for selective hydrogenation comprising, consisting essentially, or consisting of at least one Group VIII metal and at least one Group IB, IIB, VIIB, or IIIA (using the CAS classification system) metal, where the metals are deposited on a catalyst support.

The catalyst support may comprise a silica, an alumina, a silica-alumina, an aluminate, an alternate metal or alloy, a sintered or refractory oxide or carbide (including silicon carbide, tungsten carbide, and others known to those skilled in the art) or carbon. The aluminate may comprise mixed alkali metal, alkaline earth, zinc, or cadmium aluminate. The catalyst support is preferably an inorganic support and, more preferably, the catalyst support is an alumina support.

The Group VIII metal may be palladium, platinum, or nickel. The Group VIII metal is preferably palladium.

The Group IB metal may be copper, silver, or gold. The Group IB metal is preferably silver, gold, or a combination thereof. The Group VIIB metal may be manganese or rhenium. The Group VIIB metal is preferably manganese. The Group IIB metal is preferably zinc. The Group IIIA metal is preferably gallium, indium, or a combination thereof.

The present invention also provides a method for making a supported hydrogenation catalyst comprising: applying a Group VIII metal to a support to give a final concentration of from about 0.1% to about 1.0% by weight; applying a second metal to the first metal-coated support to give a final concentration of from about 0.05% to about 1.2% by weight; drying; calcining; and reducing such that the final catalyst exhibits a satisfactory conversion, selectivity, and sustained activity in liquid-phase selective hydrogenation.

The present invention also includes a catalyst as above wherein a supported Group VIII metal catalyst is obtained commercially and further prepared as described herein.

The present invention further provides a method for screening or evaluating the suitability of catalysts for selective hydrogenation, particularly for screening the catalysts on the basis of estimated or relative conversion, selectivity, and sustained activity. This method provides steps including (among others) applying one or more promoters to a supported Group VIII catalyst, preparing a

reactant stream comprising acetylene in NMP, contacting the reactant stream and a hydrogen/carbon monoxide stream with both reference and test catalysts, and measuring product concentrations in steady-state liquid phase hydrogenation of acetylene, from which catalyst performance can be evaluated.

5 The present invention also includes a process for selective hydrogenation using the catalyst(s), catalyst preparation method(s), and catalyst screening method(s), all described in more detail herein.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 A preferred embodiment of the present invention provides a catalyst for selective hydrogenation comprising, consisting essentially, or consisting of at least one Group VIII metal and at least one Group IB, IIB, VIIB, or IIIA (CAS nomenclature) metal, which may be gallium, indium, silver, manganese, or zinc, where the metals are deposited on a catalyst support.

Another preferred embodiment of the present invention is a method for catalyst preparation, comprising: impregnating the support with a solution of a Group VIII metal compound or precursor, 15 the metal concentration of the Group VIII metal compound or precursor preferably being chosen so that 0.01 to 10% of the Group VIII metal is fixed on the support; drying; calcining at 110°C to 600°C; reducing at 100°C to 400°C; impregnating with a solution of at least one of Group IB, IIB, VIIB, or IIIA metals or precursors, the metal or precursor concentration(s) preferably being chosen so that 0.01 to 10% of the at least one of Group IB, IIB, VIIB, or IIIA metals is fixed on the support; 20 drying; calcining at 110°C to 600°C; and reducing at 100°C to 400°C. The metals may preferably be applied to the support in any order.

In another preferred embodiment, the impregnating solution may comprise both the Group VIII metal compound or precursor and the at least one of Group IB, IIB, VIIB, or IIIA metals or precursors, such that the metals are preferably applied to the support together and at the same time. 25 In this embodiment, the drying, calcining, and reducing steps may preferably be conducted once.

Another preferred embodiment of the present invention includes a catalyst for selective hydrogenation wherein a supported Group VIII metal catalyst is obtained commercially and further prepared as described herein preferably by wet impregnation with a promoter metal or metal precursor, although the promoter metal may be applied by any technique known in the art without 30 departing from the scope of the invention.

The reducing gas is preferably hydrogen or a hydrogen-containing gas, as will be known to those of skill in the art, and may also contain carbon monoxide or a carbon monoxide-containing gas. Both the drying and calcining steps may take place in oxygen-containing or substantially oxygen-free environments.

The catalyst support is preferably an alumina, but may also be a silica, a silica-alumina, an aluminate, an alternate metal or alloy, a sintered or refractory oxide or carbide (including silicon carbide, tungsten carbide, and others known to those skilled in the art) or carbon. The aluminate may be mixed alkali metal, alkaline earth, zinc or cadmium aluminate. The Group VIII metal is preferably palladium but may also be platinum, or nickel. The Group IB metal may be copper, silver, or gold. The Group VIIB metal may be manganese or rhenium. The Group IIIA metal may be indium or gallium. The Group IIB metal may be zinc.

The Group IB or IIB metal concentration is preferably 0.01 to 10% by weight. The Group VIIB metal concentration is preferably 0.01 to 10% by weight. The Group IIIA metal concentration is preferably 0.01 to 10% by weight. The molar ratio of the group IB or IIB metal to group VIII metal may be from about 0.1 to about 10. The molar ratio of the group VIIB metal to group VIII metal may range from about 0.1 to about 10. The molar ratio of the group IIIA metal to group VIII metal may range from about 0.1 to about 10.

The present invention also includes catalysts in which the metal support may comprise a wire, wire mesh, powder, or shot composed of palladium, platinum, nickel, tungsten, tantalum, columbium, molybdenum, chromium, vanadium, titanium, iron, cobalt, carbon, and/or an alloy containing any or all of these elements. The sintered refractory oxide may be tantalum oxide, dysprosium oxide, titanium dioxide, ytterbium oxide, yttrium oxide, gadolinium oxide, and zirconium oxide.

In another preferred embodiment, the present invention further includes a method for screening or evaluating the suitability of catalysts for selective hydrogenation, particularly for screening the catalysts on the basis of estimated or relative conversion and selectivity.

In another preferred embodiment, the present invention further includes the application of catalysts as described herein to selective conversion of acetylenic compounds to ethylenic compounds comprising the charging of a feedstream containing the acetylenic compound or compounds to a single pass, continuous reactor containing the catalyst and operated at conditions conducive to hydrogenation. The acetylenic compound may be a gas and the reactor may be operated such that the fluid media in the reactor is in the gas or supercritical fluid phase form. The acetylenic compound may alternatively be a liquid and distributed as a component of a stream wholly or mostly in the gas state at reactor operating conditions such that the fluid media in the reactor is in a gas, supercritical, or mixed phase form. Further alternatively, the acetylenic compound may be a liquid and distributed as a component of a stream wholly or mostly in the liquid state at reactor operating conditions such that the fluid media in the reactor is in the liquid, supercritical, or mixed phase form. Also, the acetylenic compound may be a gas at reactor operating

conditions and distributed as a component of a stream wholly or mostly in the liquid state such that the fluid media in the reactor is in a liquid, supercritical, or mixed phase form.

In another preferred embodiment, the present invention provides a process for the use of the inventive catalysts as described in our co-filed application Ser.No. \_\_/\_\_\_\_\_, entitled "Process for Liquid Phase Hydrogenation" by Marvin M. Johnson, Edward R. Peterson, and Sean C. Gattis, hereby incorporated by reference herein in its entirety.

The acetylenic compound will typically be absorbed in a non-hydrocarbon solvent, and the non-hydrocarbon solvent may be a polar solvent including, but not limited to: n-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and monomethylamine (MMA).

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

## EXAMPLES

### *Catalyst Preparation*

A number of experimental catalysts were prepared by incipient wetness impregnation of a commercially available "skin" catalyst (also known in the art as "rim" or "eggshell" catalysts) that contained from 0.3 to 0.7 wt-% palladium concentrated near the exterior surface of roughly spherical particles of alumina, which had been heat treated to reduce microporosity. For example, a commercially available catalyst originally available from Mallinckrodt Chemicals, product number E144SDU, containing about 0.5 wt-% Pd on roughly spherical 1/16" diameter alumina particles, with a surface area of about 40-70 m<sup>2</sup>/gm and a pore volume of about 0.5 may be used. Similar catalysts commercially available from Engelhard and Calsicat (such as 1435DU) may also be used. Several of the experimental catalysts described below were crushed and then double-screened between 40 and 50 mesh (USS or U.S. sieve series) screens, thus providing catalyst particles with a minimum dimension in the range of from about 0.0117 to about 0.0165 inches. Those skilled in the art will recognize that other known catalysts and supports may likewise be employed without departing from the scope of the invention. Most of the experimental catalysts described below involved dissolving the nitrate salt of the promoter in the amount of water required to just fill the internal pores of the catalyst support, though other techniques as are known in the art may of course be employed.

## Example 1

## (Comparative)

Catalyst containing 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. A commercially available Engelhard catalyst that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub> was used for this Example. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was dried for one hour. The dried product was reduced in place at 100 °C and 250 psig for two hours with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

## Example 2

## (Comparative)

Catalyst containing 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began with the Engelhard catalyst of Example 1 that contained 0.3 wt-% Pd/ Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was dried for one hour, crushed and double-screened between 40 and 50 mesh (USS) screens, and reduced in place at 400 °C and 150 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

## Example 3

## (Comparative)

Catalyst containing 0.7 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began with an Engelhard catalyst which contained 0.7 wt-% Pd/ Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The catalyst was reduced in place at 50 °C and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

## Example 4

Catalyst containing 0.3 wt-% Pd - 1.2 wt-% Au/Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began with the Engelhard catalyst of Example 1 that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst particles were dropwise impregnated with a gold chloride solution, dried at 150°C for one hour, and calcined at 300°C for one hour to produce a 1.2 wt-% Au - 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub> product. The product was crushed and double-screened between 40 and 50 mesh (USS) screens, and reduced in place for one hour at 100 °C and 250 psig with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

## Example 5

Catalyst containing 0.3 wt-% Pd - 0.3 wt-% Ag/ Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began with a Calsicat catalyst that contained 0.3 wt-% Pd/ Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this Example, 10 grams of the Calsicat catalyst was dropwise impregnated with 0.047 grams of AgNO<sub>3</sub> dissolved in 5 ml of

water, dried for one hour at 150 °C, and calcined at 300°C for one hour to give a 0.3% Ag - 0.3% Pd/  
Al<sub>2</sub>O<sub>3</sub> product. The product was then crushed and double screened between 40 and 50 mesh (USS)  
screens and reduced in place at 100°C and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66%  
H<sub>2</sub> - 34% CO).

#### Example 6

Catalyst containing 0.3 wt-% Pd – 0.6 wt-% Ag/Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began  
with the Calsicat catalyst of Example 5 that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported  
catalyst particles were roughly spherical and approximately 1/16 inches in diameter. For this  
Example, the procedure of Example 5 was followed except that the concentration of silver nitrate in  
the impregnating solution was twice that of Example 5. The product was again dried for one hour at  
150°C, and calcined at 300°C for one hour. The 0.6% Ag - 0.3% Pd/ Al<sub>2</sub>O<sub>3</sub> product was then  
crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 100°C  
and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

#### Example 7

Catalyst containing 0.3 wt-% Pd – 0.1 wt-% Mn/Al<sub>2</sub>O<sub>3</sub>. This catalyst was prepared from an  
Engelhard catalyst that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were  
roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was  
dropwise impregnated with manganese acetate, dried at 150°C and calcined at 300°C to give a 0.3  
wt-% Pd - 0.1 wt-% Mn/Al<sub>2</sub>O<sub>3</sub> product. The calcined product was then crushed and double screened  
between 40 and 50 mesh (USS) screens, and reduced in place at 300°C and 250 psig for one hour  
with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

#### Example 8

Catalyst containing 0.3 wt-% Pd – 0.385 wt-% In/Al<sub>2</sub>O<sub>3</sub>. This catalyst was prepared from the  
Engelhard catalyst that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were  
roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was  
dropwise impregnated with an aqueous solution of indium nitrate, dried at 150°C for one hour, and  
calcined at 300 °C for one hour to give a 0.3 wt-% Pd - 0.4 wt-% In/Al<sub>2</sub>O<sub>3</sub> product. The calcined  
product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced  
in place at 300-314°C and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

#### Example 9

Catalyst containing 0.3 wt-% Pd – 0.26 wt-% Ga/Al<sub>2</sub>O<sub>3</sub>. This catalyst was prepared from the  
Engelhard catalyst that contained 0.3 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were  
roughly spherical and approximately 1/16 inches in diameter. For this Example, the catalyst was  
dropwise impregnated with an aqueous solution of gallium nitrate, dried at 150°C for one hour, and

calcined at 300°C for one hour to give 0.3 wt-% Pd - 0.26 wt-% Ga/Al<sub>2</sub>O<sub>3</sub> product. The product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 400°C and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

#### Example 10

5        Catalyst containing 0.5 wt-% Pd - 0.5 wt-% Zn/Al<sub>2</sub>O<sub>3</sub>. Preparation of this catalyst began with a palladium catalyst from Calsicat (product number E144SDU) containing 0.5 wt-% Pd/Al<sub>2</sub>O<sub>3</sub>. The alumina supported catalyst particles were roughly spherical and approximately 1/16 inches in diameter. The palladium-containing material was then dropwise impregnated with a solution of zinc formate, dried for one hour at 150°C, and calcined at 300°C for one hour to give a 0.5 wt-% Pd - 0.5  
10 wt-% Zn/Al<sub>2</sub>O<sub>3</sub> product. The product was then crushed and double screened between 40 and 50 mesh (USS) screens, and reduced in place at 400-420°C and 250 psig for one hour with a 2:1 H<sub>2</sub>:CO gas mixture (66% H<sub>2</sub> - 34% CO).

#### *Catalyst Selective Hydrogenation Screening Tests*

#### Example 11

15        A reaction vessel constructed of one-half inch (OD) stainless steel tube was used for these tests. Approximately 3 cm<sup>3</sup> of catalyst was diluted with 6 cm<sup>3</sup> of inert low surface area alumina (alundum) as a catalyst surface area diluent, and placed into the reactor in a fixed bed configuration. Other catalyst surface area diluents may of course be used, as will be known to those skilled in the art. The catalyst was placed in the center section of the reactor between two six-inch deep beds of 3  
20 mm glass beads, one placed upstream of the catalyst for preheat purposes and one downstream, in the exit section. A 1/8" diameter thermowell was located near the center of the reactor, thus the reaction temperature was measured near the center of the catalyst bed.

The operating conditions are as shown in Table 1. The liquid reactant flow rate was set at 18 ml/hr of NMP containing 4.2 wt-% dissolved acetylene. A 2:1 H<sub>2</sub>:CO gas mixture was used and the  
25 H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratio was 1.56:1. Product gas analyses (for C<sub>2</sub> components only) were obtained after the composition of the product gas, which was taken from a knockout pot that collected virtually all of the NMP, had reached steady state and subsequent samples showed no significant change in composition. The gas composition results are shown in Table 1. The product gas concentrations do not sum to 100% due to the presence of other components in minor amounts and measurement error.  
30 Because these were catalyst screening tests, it is estimated that the mass balance closure for these results was about 95%.

For purposes of comparing the performance of the catalyst formulations tested, the selectivity of ethylene to ethane may be estimated by the ratio of the product ethylene concentration to the concentration of ethane, defined here as the screening selectivity  $S_s$  (and presented in Table 1) as  $S_s =$



$[C_2H_4] / [C_2H_6]$ . Also for comparison purposes, the relative acetylene conversions may be estimated from the product acetylene concentrations. This is defined here (and also presented in Table 1) as the screening conversion  $S_c = 100 - [C_2H_2]$  where the acetylene concentration is expressed in percent.

The data shown in Table 1 thus describe representative results for promoted Group VIII selective hydrogenation catalysts made and used in accordance with the invention. As may be seen from examination of the data tabulated in Table 1, significant improvements in the selectivity to ethylene result from the addition of promoters at high acetylene conversion. Contrary to the teachings of the prior art, a progressive decline in activity with time on stream was not observed, and the gallium and indium containing catalysts showed relatively high selectivity. Likewise, excellent selectivity and activity were observed for the catalysts of the invention obtained by applying a promoter metal after first applying the Group VIII metal to the support. Accordingly, the catalysts of the present invention are effective in the selective hydrogenation of acetylene. The indium-promoted catalyst and, to a lesser extent, the gallium-promoted catalyst is effective with palladium on alumina, and exhibit higher selectivity to ethylene than either the silver-promoted or gold-promoted catalysts traditionally used to advantage for the removal of small amounts of acetylene in ethylene by selective hydrogenation in the front-end gas phase hydrogenation process.

Table 1

Catalyst	Composition	T (°C)	P (psig)	H <sub>2</sub> /CO Flow (ml/min)	Ethane (%)	Ethylene (%)	Acetylene (%)	$S_s$	$S_c$ (%)
Example 1	0.3% Pd on 1/16" alumina spheres	111	250	30	10.0	89.4	0.5	8.9	99.5
Example 2	0.3% Pd on 40-50 mesh alumina particles	128	150	35	2.6	94.0	0.80	36	99.2
Example 3	0.7% Pd on 1/16" alumina spheres	111	250	40	6.4	93.4	0.1	15	99.9
Example 4	0.3% Pd – 1.2% Au on 40-50 mesh alumina particles	120	250	35	6.25	93.50	0.15	15	99.9
Example 2	0.3% Pd on 40-50 mesh alumina particles	119	250	32	2.42	91.0	6.34	38	93.7
Example 5	0.3% Pd – 0.3% Ag on 40-50 mesh alumina particles	114	250	30	3.68	93.5	2.77	25	97.2
Example 6	0.3% Pd – 0.6% Ag on 40-50 mesh alumina particles	115	250	30	3.33	96.2	0.41	29	99.6
Example 7	0.3% Pd – 0.1% Mn on 40-50 mesh alumina particles	122	250	30	3.91	95.6	0.42	24	99.6
Example 8	0.3% Pd – 0.385% In on 40-50 mesh alumina particles	137	250	30	1.46	96.8	1.70	66	98.3
Example 9	0.3% Pd – 0.26% Ga on 40-50 mesh alumina particles	130	250	30	2.02	97.5	0.40	48	99.6

**Selective Hydrogenation - Sustained Activity Tests****Example 12**

The results obtained from Example 11 and shown in Table 1 were considered promising. Therefore, an extended duration run was made with an indium-containing catalyst similar to that of Example 8 but with 0.22 wt-% indium to determine whether this high selectivity catalyst would also have sustained activity for selective hydrogenation. Operating conditions for the sustained activity tests included: reactor pressure of 150 psig; 1.5 wt-% acetylene was absorbed and dissolved in the NMP absorbent to provide the reactant stream; the molar ratio of H<sub>2</sub> to C<sub>2</sub>H<sub>2</sub> was set at 1.26:1; and the flowrate of reactant through the bed (liquid hourly space velocity) was set to an LHSV of 5 hr<sup>-1</sup>.

The catalyst was operated for about 143 hours, and product gas composition was determined at selected intervals, as shown in Table 2. It is estimated that the mass balance closure for these results was about 95 %.

**Table 2**

Time on Stream (hrs)	70	104
Temperature (°C)	134	134
Pressure (psig)	150	150
Methane (wt-%)	0.01	0.01
Ethane (wt-%)	1.30	1.19
Ethylene (wt-%)	97.50	98.10
Acetylene (wt-%)	0.39	0.08
Trans-2-butene (wt-%)	0.07	0.06
1-butene (wt-%)	0.21	0.17
Cis-2-butene (wt-%)	0.07	0.06
Butadiene (wt-%)	0.40	0.31
Total (wt-%)	99.95	99.98
<i>S<sub>s</sub></i>	75	82
<i>S<sub>c</sub></i> (%)	99.6	99.9

After this extended run, the catalyst bed was flushed with nitrogen at 425°C and the catalyst was oxidized in air for one hour. The catalyst was then reduced with the 2:1 H<sub>2</sub>:CO mixture at 417°C and 150 psig, and tested again to determine whether it was active. The catalyst was again both active and selective for the selective hydrogenation of acetylene dissolved in NMP with a H<sub>2</sub> and CO mixture.

**Zinc-Promoted Catalyst****Example 13**

This example was performed under conditions similar to those of Example 11, using the catalyst prepared as described in Example 10. The reactant stream comprised 1.5 wt-% acetylene in

NMP. The  $\text{H}_2:\text{CO}$  feed ratio was 2:1 (vol/vol). The  $\text{H}_2:\text{C}_2\text{H}_2$  to the reactor was 2.76:1. The reaction pressure was maintained at approximately 250 psig and the average temperature in the catalyst bed was  $128^\circ\text{C}$ . The reactant stream flowrate was set to a LHSV of  $5\text{ hr}^{-1}$ .

Table 3 provides results from these tests in the form of product gas composition as a function of reaction time. It is estimated that the mass balance closure for these results was about 98-99 %. As will be seen from the results in Table 3, the zinc-promoted catalyst provides improved ethylene selectivity at high acetylene conversion.

Table 3

Time (hr)	$\text{CH}_4$ (wt-%)	$\text{C}_2\text{H}_6$ (wt-%)	$\text{C}_2\text{H}_4$ (wt-%)	$\text{C}_2\text{H}_2$ (wt-%)	t- $\text{C}_4\text{H}_8$ (wt-%)	i- $\text{C}_4\text{H}_8$ (wt-%)	c- $\text{C}_4\text{H}_8$ (wt-%)	1,3- $\text{C}_4\text{H}_8$ (wt-%)	$S_s$	$S_c$ (%)
0.5	0.04	0.91	97.4	0.48	0.04	0.09	0.07	0.85	107	99.5
1.0	0.02	0.87	97.4	0.37	0.05	0.09	0.08	1.00	112	99.6
1.5	0.02	0.85	97.5	0.29	0.05	0.09	0.07	1.00	115	99.7
2.0	0.01	0.84	97.6	0.24	0.04	0.09	0.07	1.00	115	99.8
2.5	0.01	0.83	97.7	0.21	0.04	0.08	0.06	0.97	118	99.8
3.0	0.01	0.82	97.8	0.20	0.04	0.08	0.06	0.93	119	99.8
3.5	0.01	0.81	97.9	0.18	0.04	0.07	0.06	0.89	121	99.8
4.0	0.01	0.81	98.0	0.16	0.03	0.07	0.05	0.83	121	99.8
4.5	0.01	0.80	98.1	0.14	0.03	0.07	0.05	0.77	123	99.9
5.0	0.01	0.79	98.2	0.12	0.03	0.06	0.04	0.72	124	99.9

### Sustained Activity - Zinc-Promoted Catalyst

#### Example 14

This example was again performed using the catalyst of Example 10. The test was performed under conditions similar to those of Example 13 but with the following differences. The reactant stream flowrate was set to a LHSV of  $10\text{ hr}^{-1}$ . The average catalyst bed temperature was  $140^\circ\text{C}$ , and the  $\text{H}_2:\text{C}_2\text{H}_2$  to the reactor was 3.7:1.

The results of this test are provided in Table 4 in the form of gas composition. The gas composition data are the result of gas analyses only; when the  $\text{C}_4$  compounds that collect in the liquid are combined with those in the gas phase, 3.14 wt-% of the acetylene reacted goes to form  $\text{C}_4$  compounds initially, but this figure drops to 2.31 wt-% after 14 hours of operation and levels off to about 2.1 wt-% after about 21 hours of operation. It is estimated that the mass balance closure for these results was about 98%-99%.

Accordingly, the progressive decline in activity with time on stream predicted by the conventional art is not observed. Further, the results of Table 3 indicate improvement in selectivity with time on stream for the catalyst of Example 10.

Table 4

Time (hr)	CH <sub>4</sub> (wt-%)	C <sub>2</sub> H <sub>6</sub> (wt-%)	C <sub>2</sub> H <sub>4</sub> (wt-%)	C <sub>2</sub> H <sub>2</sub> (wt-%)	C <sub>4</sub> H <sub>8</sub> (wt-%)	1,3- C <sub>4</sub> H <sub>8</sub> (wt-%)	S <sub>s</sub>	S <sub>c</sub> (%)
7	0.06	0.33	97.4	1.20	0.07	0.87	295	98.8
14	0.07	0.60	98.1	0.68	0.10	0.43	164	99.3
21	0.02	0.60	98.2	0.77	0.02	0.31	164	99.2
24	0.02	0.50	98.6	0.33	0.02	0.38	197	99.7

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modification thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process design criteria, pendant processing equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Description of the Related Art is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

**WE CLAIM:**

1. A selective hydrogenation catalyst consisting essentially of:  
a precursor comprising at least one Group VIII metal disposed on an inorganic support;  
a second metal selected from the group consisting of Group IB metals, Group IIB metals,  
5 Group IIIA metals, Group VIIB metals, and combinations thereof, disposed on the precursor;  
wherein the catalyst is capable of selectively hydrogenating acetylene with a conversion  $S_c$  of  
at least about 95% and a selectivity to ethylene relative to ethane  $S_s$  of at least about 25 when the  
catalyst is employed in a steady-state liquid phase hydrogenation process.
2. The catalyst of claim 1 wherein the inorganic support comprises alumina.
- 10 3. The catalyst of claim 2 wherein the inorganic support comprises a particulate support.
4. The catalyst of claim 1 wherein the at least one Group VIII metal comprises palladium.
5. The catalyst of claim 4 wherein the second metal is selected from the group consisting of  
Group IIB metals, and combinations thereof.
6. The catalyst of claim 5 wherein the second metal comprises Zn.
- 15 7. The catalyst of claim 4 wherein the second metal is selected from the group consisting of  
Group IB metals, and combinations thereof.
8. The catalyst of claim 4 wherein the second metal is selected from the group consisting of  
Group VIIB metals, and combinations thereof.
9. The catalyst of claim 8 wherein the second metal comprises Mn.
- 20 10. The catalyst of claim 4 wherein the second metal is selected from the group consisting of  
Group IIIA metals, and combinations thereof.
11. The catalyst of claim 10 wherein the second metal is selected from the group consisting of In,  
Ga, and combinations thereof.
12. The catalyst of claim 4 wherein the second metal is selected from the group consisting of In,  
25 Ga, Mn, Zn, and combinations thereof.
13. The catalyst of claim 12 wherein the catalyst is capable of sustained activity for acetylene  
hydrogenation for at least about 150 hours.
14. A composition comprising:  
a support;  
30 a Group VIII metal disposed on the support;  
a second metal selected from the group consisting of Group IIIA metals, Group IIB metals,  
Group VIIB metals, and combinations thereof, disposed on the support;  
said composition characterized by substantially sustained activity for selective  
hydrogenation.

15. The composition of claim 14 wherein said sustained activity for selective hydrogenation comprises sustained activity for liquid-phase selective hydrogenation.

16. The composition of claim 15 wherein said selective hydrogenation comprises selective hydrogenation of acetylene.

5 17. The composition of claim 16 wherein the activity is sustainable for at least about 150 hours.

18. The composition of claim 16 further comprising a selectivity of ethylene relative to ethane  $S_s$  greater than or equal to about 25.

19. The composition of claim 18 further comprising an acetylene conversion  $S_c$  of about 95% or greater.

10 20. The composition of claim 16 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

21. The composition of claim 20 wherein the second metal comprises Mn.

22. The composition of claim 15 wherein the concentration of said Group VIII metal is within the range of from about 0.1 wt-% to about 1.0 wt-%.

15 23. The composition of claim 22 wherein the concentration of said Group VIII metal is within the range of from about 0.2 wt-% to about 0.8 wt-%.

24. The composition of claim 23 wherein the concentration of said Group VIII metal is within the range of from about 0.2 wt-% to about 0.5 wt-%.

20 25. The composition of claim 22 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 2.0 wt-%.

26. The composition of claim 25 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 1.2 wt-%.

27. The composition of claim 26 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 1.0 wt-%.

25 28. The composition of claim 27 wherein the concentration of said second metal is within the range of from about 0.05 wt-% to about 0.5 wt-%.

29. The composition of claim 28 wherein the concentration of said second metal is within the range of from about 0.1 wt-% to about 0.5 wt-%.

30 30. The composition of claim 29 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

31. The composition of claim 30 wherein the second metal comprises Mn.

32. The composition of claim 29 wherein the Group VIII metal comprises Pd.

33. The composition of claim 32 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

34. The composition of claim 33 wherein the second metal comprises Mn.
35. The composition of claim 33 wherein the second metal comprises In or Ga.
36. The composition of claim 33 wherein the second metal comprises Zn.
37. A catalyst active for liquid-phase selective hydrogenation comprising:  
5 Pd supported on particulate alumina;  
a subsequently supported second metal selected from the group consisting of Ga, In, Mn, Zn, and combinations thereof;  
a once-through acetylene conversion  $S_c$  of at least about 95%; and  
a selectivity for ethylene relative to ethane  $S_s$  of at least about 40.
- 10 38. The catalyst of claim 37 further comprising a sustained activity for selective hydrogenation of at least 150 hours.
39. The catalyst of claim 38 wherein the second metal comprises from about 0.05 % to about 1 % of the catalyst by weight.
40. The catalyst of claim 39 wherein the Pd comprises from about 0.1 % to about 1.0 % of the  
15 catalyst by weight.
41. The catalyst of claim 40 wherein the Pd comprises from about 0.2 % to about 0.5 % of the catalyst by weight.
42. The catalyst of claim 39 wherein the second metal comprises from about 0.05 % to about 0.5 % of the catalyst by weight.
- 20 43. The catalyst of claim 42 wherein the Pd comprises from about 0.1 % to about 1.0 % of the catalyst by weight.
44. The catalyst of claim 43 wherein the Pd comprises from about 0.2 % to about 0.5 % of the catalyst by weight.
45. The catalyst of claim 44 wherein the second metal is Mn.
- 25 46. The catalyst of claim 44 wherein the second metal is In or Ga.
47. The catalyst of claim 44 wherein the second metal is Zn.
48. The catalyst of claim 38 wherein the second metal is Mn.
49. The catalyst of claim 38 wherein the second metal is In or Ga.
50. The catalyst of claim 38 wherein the second metal is Zn.
- 30 51. A supported catalyst for selective hydrogenation comprising:  
a Group VIII metal;  
a second metal selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof; and  
a single-pass conversion  $S_c$  of at least 90% in liquid-phase hydrogenation of acetylene.

52. The catalyst of claim 51 wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.

53. The catalyst of claim 52 further comprising a selectivity for ethylene relative to ethane  $S_s$  of at least 40.

5 54. The catalyst of claim 53 wherein the second metal comprises about 0.05 wt-% to 1.0 wt-% of the catalyst by weight.

55. The catalyst of claim 54 wherein the second metal comprises about 0.1 wt-% to 0.5 wt-% of the catalyst by weight.

10 56. The catalyst of claim 55 further comprising a sustained activity for selective hydrogenation of acetylene of about 150 hours or greater.

57. The catalyst of claim 56 wherein the second metal is selected from the group consisting of Ga, Mn, In, Zn, and combinations thereof.

58. The catalyst of claim 57 wherein the Group VIII metal and the second metal are applied to the catalyst sequentially.

15 59. The catalyst of claim 58 wherein the second metal is applied to the catalyst after the Group VIII metal.

60. The catalyst of claim 57 wherein the second metal and the Group VIII metal are applied to the catalyst at about the same time.

61. The catalyst of claim 59 wherein the Group VIII metal is Pd.

20 62. The catalyst of claim 61 wherein the catalyst comprises an alumina support.

63. The catalyst of claim 62 wherein the support is a particulate support.

64. The catalyst of claim 63 wherein the particles have a minimum dimension between about 0.01 in. and about 0.2 in.

25 65. The catalyst of claim 64 wherein the particles have a minimum dimension between about 0.01 in. and about 0.02 in.

66. A supported catalyst for selective hydrogenation comprising:

a first metal selected from the group consisting of Group VIII metals and combinations thereof;

30 a second metal selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof; and

an ethylene selectivity relative to ethane  $S_s$  of at least 20 in liquid-phase hydrogenation of acetylene.

67. The catalyst of claim 66 wherein the ratio of the amounts of the first metal to the second metal in the catalyst is from about 6 to about 0.25.



68. The catalyst of claim 67 wherein the ratio of the amounts of the first metal to the second metal in the catalyst is from about 3 to about 0.5.
69. The catalyst of claim 68 wherein the Group VIII metal is palladium.
70. The catalyst of claim 69 wherein the second metal is Zn.
- 5 71. The catalyst of claim 69 wherein the second metal is Mn.
72. The catalyst of claim 69 wherein the second metal is selected from the group consisting of Group IIIA metals and combinations thereof.
73. The catalyst of claim 72 wherein the second metal is selected from the group consisting of In, Ga, and combinations thereof.
- 10 74. The catalyst of claim 73 wherein the ethylene selectivity relative to ethane  $S_s$  is greater than 40.
75. The catalyst of claim 74 further comprising a sustained activity in selective hydrogenation of greater than 100 hours.
76. The catalyst of claim 75 further comprising an acetylene conversion  $S_c$  greater than or equal  
15 to 90%.
77. The catalyst of claim 76 further comprising an acetylene conversion  $S_c$  greater than 95%.
78. A method of screening catalysts for liquid-phase selective hydrogenation comprising:  
preparing a test catalyst by adding a promoter selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof, to a  
20 reference catalyst comprising a supported Group VIII metal catalyst precursor;  
preparing a liquid reactant stream comprising between 1 wt-% and 10 wt-%  $C_2H_2$  dissolved in n-methyl-2-pyrrolidone;  
testing the test catalyst and the reference catalyst by contacting the reactant stream and an  
approximately 2:1  $H_2:CO$  gas mixture in continuous flow with the test catalyst and reference  
25 catalyst, respectively, at a feed ratio of  $H_2:C_2H_2$  of from about 1:1 to about 4:1 at selective  
hydrogenation reaction conditions to produce a product stream,  
condensing substantially all of the n-methyl-2-pyrrolidone from the product stream;  
measuring the concentrations of products comprising  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  in the product  
stream at steady state;  
30 determining performance parameters for the test catalyst and the reference catalyst  
comprising the respective  $C_2H_2$  conversion  $S_c$  and  $C_2H_4$  selectivity relative to  $C_2H_6$   $S_s$ ;  
comparing the test catalyst performance parameters to those for the reference catalyst.

79. The method of claim 78 wherein said selective hydrogenation reaction conditions comprise a temperature in the range of about 100°C to about 150°C, and a pressure of from about 150 psig to about 250 psig.

80. The method of claim 79 further comprising diluting the test catalyst and reference catalyst with a catalyst surface area diluent.

81. The method of claim 80 wherein said catalyst surface area diluent comprises alumina.

82. The method of claim 81 wherein the catalyst support is a particulate support.

83. The method of claim 82 wherein testing is performed using a liquid phase reactant stream comprising from about 1.0 wt-% to about 5.0 wt-% C<sub>2</sub>H<sub>2</sub> dissolved in n-methyl-2-pyrrolidone.

84. A method of making a promoted catalyst for selective hydrogenation comprising:

impregnating a carrier by incipient wetness impregnation with an aqueous solution of a promoter selected from the group consisting of Group IB metals, Group IIB metals, Group IIIA metals, Group VIIB metals, and combinations thereof, in a concentration sufficient to deposit the promoter on the carrier in a finished concentration of from about 0.05 wt-% to about 1.0 wt-%;

drying the product of the impregnation for about one hour at about 150°C;

calcining the dried product at about 300°C;

reducing the calcined product for 1 – 2 hours at a temperature in the range of from about 100°C to about 425°C in an atmosphere consisting of an approximately 2:1 mixture of H<sub>2</sub>:CO at a pressure of from about 150 psig to about 250 psig.

85. The method of claim 84 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.

86. The method of claim 85 wherein the promoter is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.

87. The method of claim 86 wherein the promoter is Mn or Zn.

88. The method of claim 87 wherein the carrier comprises a Group VIII metal disposed on a support.

89. The method of claim 88 wherein the support comprises particulate alumina.

90. The method of claim 89 wherein the finished concentration of the Group VIII metal is within the range of 0.1 wt-% to 10 wt-%.

91. The method of claim 90 wherein the Group VIII metal is Pd.

92. The method of claim 91 wherein the finished concentration of Pd is within the range of 0.2 wt-% to 0.8 wt-%.

93. The method of claim 92 wherein the finished concentration of Pd is from about 0.2 wt-% to about 0.5 wt-%.

94. The method of claim 92 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.
95. The method of claim 94 wherein the promoter is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
- 5 96. The method of claim 95 wherein the promoter is Mn or Zn.
97. The method of claim 95 wherein the aqueous solution comprises an aqueous solution of the nitrate salt of the promoter, and the reduction is carried out at about 400-420°C for about one hour.
98. The method of claim 84 wherein the promoter is selected from the group consisting of Group IB metals and combinations thereof, the aqueous solution comprises an aqueous solution of a salt of
- 10 the promoter, and the reduction is carried out at about 100°C for about two hours.
99. The method of claim 84 further comprising impregnating the carrier by incipient wetness impregnation with a solution comprising a metal selected from the group consisting of Group VIII metals and combinations thereof, in a concentration sufficient to deposit the metal on the carrier in a finished concentration of from about 0.1 wt-% to about 5.0 wt-%.
- 15 100. The method of claim 99 wherein the impregnation steps are performed simultaneously.
101. The method of claim 100 wherein the promoter is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof.
102. The method of claim 101 wherein the promoter is selected from the group consisting of In, Ga, Mn, Zn, and combinations thereof.
- 20 103. The method of claim 102 wherein the promoter is Mn or Zn.
104. The method of claim 102 wherein the carrier comprises alumina.
105. The method of claim 104 wherein the alumina comprises particulate alumina.
106. The method of claim 105 wherein the Group VIII metal is Pd.
107. The method of claim 106 wherein the finished concentration of Pd is from about 0.1 wt-% to
- 25 about 1.0 wt-%.
108. The method of claim 107 wherein the promoter is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.
109. The method of claim 108 wherein the promoter is Mn or Zn.
110. A catalyst made in accordance with the method of claim 95.
- 30 111. A catalyst made in accordance with the method of claim 109.
112. A hydrogenation catalyst made by a process comprising:  
applying a first metal to a support;  
applying a second metal to the support;  
drying the first and second metal-coated support;

calcining the dried first and second metal-coated support to provide a precursor;

reducing the precursor;

wherein the first metal comprises a Group VIII metal and is applied to provide 0.1% - 1.0% by weight of the first metal to final weight of the catalyst;

5        wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof, and applied to provide 0.05% - 1.2% by weight of the second metal to final weight of the catalyst;

         wherein said first and second metals are applied such that the catalyst is capable of a sustained activity for selective hydrogenation of at least 150 hours and a once-through conversion  $S_c$  of at least 95% in liquid-phase hydrogenation of acetylene.

113.    The process of claim 112 wherein the first and second metals are applied to the support concurrently.

114.    The process of claim 112 wherein the second metal is selected from the group consisting of Group IIIA metals, Group IIB metals, Group VIIB metals, and combinations thereof, and applied to provide 0.1% - 0.5% by weight of second metal to final weight of the catalyst.

115.    The process of claim 114 wherein the second metal is selected from the group consisting of Mn, In, Ga, Zn, and combinations thereof.

116.    The process of claim 115 wherein the second metal comprises Mn or Zn.

117.    The process of claim 115 wherein the first metal comprises Pd.

20    118.    The process of claim 115 further comprising reducing the precursor for 1 - 2 hours at a temperature in the range of from about 100°C to about 425°C in an atmosphere consisting of an approximately 2:1 mixture of H<sub>2</sub>:CO at about 250 psig.

119.    The process of claim 115 wherein the selective hydrogenation reaction conditions comprise a temperature in the range of about 100°C to about 150°C, and a pressure of from about 150 psig to about 250 psig.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/38870

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 31/00, 37/00, 21/04, 21/08, 21/12, 21/14, 23/00, 23/02, 23/06, 23/08, 23/40, 23/42, 20/00.  
US CL : 502/104, 110, 117, 241, 245, 253, 262, 324, 327, 329, 330, 331, 333, 334, 339, 342, 343, 346, 348.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,925,239 A (KLEIN et al) 20 July 1999 (20.07.1999), see entire document.	1-9, 12-34, 36-45, 47-48, 50-63, & 66-71
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Y		112-119
Y	US 4,812,435 A (BAIRD, JR.) 14 March 1989 (14.03.1989), see entire document.	10-11, 35, 46, 49, & 72-77
X	US 3,867,309 A (OLECK et al) 18 February 1975 (18.02.1975), see entire document.	2-6, 8-9, 12-45, 47-48, 50-63, 66-71, & 112-119
Y	US 5,176,887 A (SUBRAMANIAN et al) 05 January 1993 (05.01.1993), see entire document.	84-111
A	US 6,576,588 B2 (RYU et al) 10 June 2003 (10.06.2003), see entire document.	78-83
A	US 6,103,106 A (McVICKER et al) 15 August 2000 (15.08.2000), see entire document.	1-77 & 112-119
A	US 6,093,670 A (BROWN) 25 July 2000 (25.07.2000), see entire document.	1-77 & 84-119



Further documents are listed in the continuation of Box C.



See patent family annex.

Special categories of cited documents:	
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Cam N Nguyen

Telephone No. 571-272-1700

Jean P. P.  
Paralegal

# INTERNATIONAL SEARCH REPORT

PCT/US03/38870

## Continuation of B. FIELDS SEARCHED Item 1:

502/104, 110, 117, 241, 245, 253, 262, 324, 327, 329, 330, 331, 333, 334, 339, 342, 343, 346, 348, 355, 415, 439, 527.12.

# INTERNATIONAL SEARCH REPORT

PCT/US03/38870

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,128,306 A (DETTING et al) 07 July 1992 (07.07.1992), see entire document.	1-119
A	US 6,221,240 B1 (KLEIN et al) 24 April 2001 (24.04.2001), see entire document.	1-119
A	US 3,962,285 A (CUSUMANO) 08 June 1976 (08.06.1976), see entire document.	84-111